

X-Ray Powder Diffraction Data on Salts of α -Sulfonated Long Chain Acids

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This paper reports x-ray powder diffraction study for twenty-four salts of α -sulfonated normal long chain fatty acids. Acid and neutral sodium, potassium, lithium, cesium, calcium, magnesium, and triethanolammonium salts of α -sulfolauric, myristic, palmitic, stearic, and behenic acids were examined. The method can be used to identify and distinguish the individual salts and has possible application to the analysis of mixtures.

THE ACID and neutral salts of normal long chain α -sulfo fatty acids, of the general formulas $\text{RCH}(\text{SO}_3\text{M})\text{CO}_2\text{H}$ and $\text{RCH}(\text{SO}_3\text{M})\text{CO}_2\text{M}$, are crystalline materials over a considerable temperature range and suitable for study by x-ray powder diffraction. The salts have possible application in detergent (4,6) and lubricating grease (1) compositions. Experimental detergent bars (6) have been made either by milling together two salts of considerably different properties or by partial neutralization of a rather hard brittle acid salt with ammonia or an amine capable of forming softer and more plastic salts in the milling process.

This paper reports on x-ray diffraction investigation for twenty-four acid and neutral salts of α -sulfonated normal long chain fatty acids. The cations employed were sodium, potassium, lithium, cesium, calcium, magnesium, and triethanolammonium. The acids employed were lauric, myristic, palmitic, stearic, and behenic acids.

Experimental

The salts of the α -sulfo fatty acids were made by methods previously described (5). X-ray powder diffraction measurements were made with a General Electric XRD-3 direct recording unit,² using nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), 1° beam slit, 0.1° detector slit, medium resolution Soller slit, scanning speed 2° per minute, chart speed 60 inches per hour, linear scale, 2-second time-constant. All samples were ground in an agate mortar to minimize orientation. The ground samples were gently packed into the recess of a plastic holder 2.0 in. long, 0.5 in. wide and 0.015 in. deep.

The complete x-ray powder diffraction data for the several salts are not included herein because of the relatively large amount of space that would be required. However the data were sent to the Joint Committee on Chemical Analysis by Powder Diffraction Methods for inclusion in the X-ray Powder Data File of the American Society for Testing Materials.

Table I lists the long spacings and the solvents used in crystallization. Water was used as the crystallization medium whenever possible but it was necessary to add ethanol in some cases to obtain complete solution. Acid lithium and triethanolammonium salts were too soluble in cold water and were crystallized from 95% ethanol or chloroform. Crystallization of

TABLE I
Long Spacing and Crystallization Medium for Salts of α -Sulfonated Long Chain Acids

Name of compound	Crystallization medium	Long spacing, \AA
Sodium α -sulfolauric acid.....	Water	24.03 ± 0.03
Sodium α -sulfomyristic acid.....	Water	26.9 ± 0.1
Sodium α -sulfopalmitic acid.....	Water	30.46 ± 0.05
Sodium α -sulfostearic acid.....	Water	32.45 ± 0.15
Sodium α -sulfohehnic acid.....	20% ethanol	38.1 ± 0.1
Disodium α -sulfopalmitate.....	Water	27.61 ± 0.03
Disodium α -sulfostearate.....	Water	29.92 ± 0.03
Potassium α -sulfomyristic acid.....	Water	22.85 ± 0.05
Potassium α -sulfopalmitic acid.....	25% ethanol	25.5 ± 0.1
Potassium α -sulfostearic acid.....	Water	27.9 ± 0.1
Dipotassium α -sulfomyristate.....	Water	24.35 ± 0.05
Dipotassium α -sulfopalmitate.....	Water	27.03 ± 0.05 ; 25.2 ± 0.1
Dipotassium α -sulfostearate.....	Water	29.28 ± 0.03
Lithium α -sulfopalmitic acid.....	95% ethanol	23.8 ± 0.1
Lithium α -sulfostearic acid.....	95% ethanol	26.0 ± 0.1
Dilithium α -sulfopalmitate.....	Water	24.5 ± 0.1
Dilithium α -sulfostearate.....	15% ethanol	26.8 ± 0.1
Cesium α -sulfostearic acid.....	Water	28.3 ± 0.1
Magnesium α -sulfopalmitic acid.....	Methanol	29.50 ± 0.05
Magnesium α -sulfostearic acid.....	Methanol	30.8 ± 0.2 ; 27.9 ± 0.2
Calcium α -sulfopalmitic acid.....	Ethanol	26.8 ± 0.2 ; 25.2 ± 0.2
Calcium α -sulfostearic acid.....	Methanol	29.8 ± 0.1 ; 27.8 ± 0.1
Sodium ammonium α -sulfostearate...	Water	25.45 ± 0.1
Triethanolammonium α -sulfo-stearic acid.....	Chloroform	27.15 ± 0.05

the acid magnesium compounds from methanol rather than water was found to produce much more crystalline salts. The long spacing values are plotted as a function of the number of carbon atoms for each homologous series in Figure 1.

Results and Discussion

All compounds investigated could be identified and distinguished on the basis of the x-ray diffraction data. The x-ray powder patterns contained a large number of diffraction peaks characteristic of the highly crystalline nature of these compounds. For some compounds doublet or additional peaks were observed in the long spacing region indicating the presence of two phases. Four compounds, dipotassium α -sulfopalmitate, magnesium α -sulfostearic acid, calcium α -sulfopalmitic acid, and calcium α -sulfostearic acid showed doublets in this region; therefore two sets of long spacings are recorded in Table I. Attempts to eliminate one of the phases by further purification or by modifications in the crystallization procedure did not result in any substantial change in diffraction patterns.

It is well known (3) that if the members of a homologous series of aliphatic compounds differ by units of two carbon atoms an isomorphous series of crystals is usually obtained and the long spacings of the series increase linearly with carbon content. Examination of the long spacing data (Table I and Figure 1) for the monosodium salts of a homologous series of α -sulfo long chain fatty acids shows an average increase of 1.4 \AA for each additional carbon atom. This is greater than the expected projected distance,

¹ Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

² Mention of commercial products does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

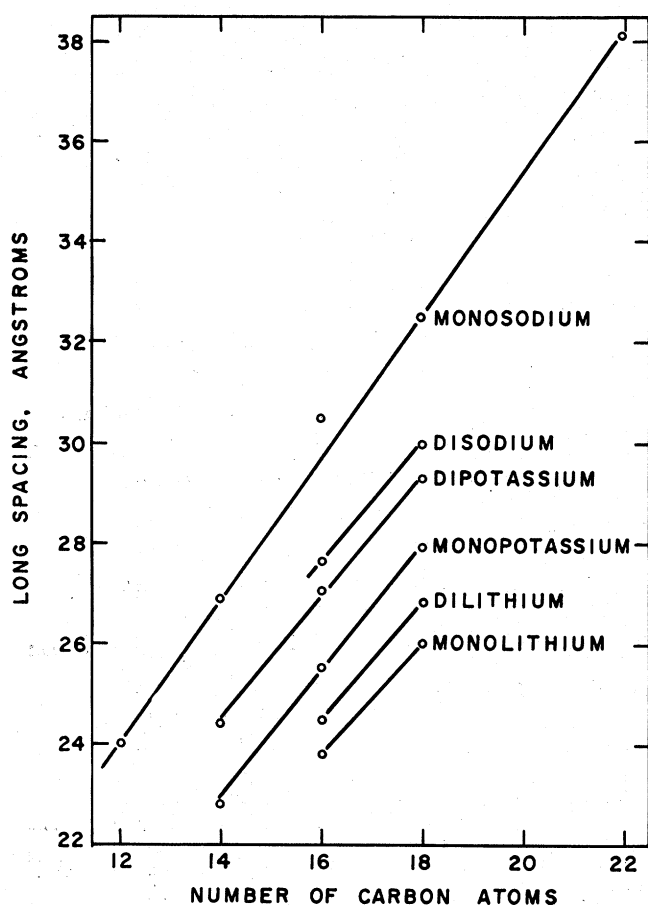


Fig. 1. Long spacings for salts of α -sulfonated acids.

1.3 Å, of a carbon-to-carbon bond. It appears that the monosodium α -sulfo fatty acids crystallize in tilted bimolecular layers characteristic of many long chain compounds. One member of the series, sodium α -sulfopalmitic acid, has a long spacing value not in accord with the other members of the series. Short spacings of the compound were within the limits of experimental error, the same as the other members of the series. Since no change in x-ray spectra was produced by extensive purification and recrystallization the reason for this irregularity is not apparent. Long spacing values for disodium α -sulfopalmitate and disodium α -sulfostearate were about 2 Å less than for the corresponding monosodium salts.

Potassium α -sulfomyristic acid, potassium α -sulfopalmitic acid, and potassium α -sulfostearic acid gave long spacing values that increased linearly with increasing chain length. The average increase for each additional carbon atom was 1.25 Å, much less than the value of 1.4 Å obtained with the monosodium salts. Apparently the molecular packing in the two salt series is quite different. The dipotassium salts gave long spacings greater than for corresponding monopotassium salts. Although one member, dipotassium α -sulfopalmitate, showed two phases, the long spacing of one phase, 27 Å, indicated that it was isomorphous with the other two members of the series.

Two members of monolithium and dilithium salts were investigated. The long spacings of the disalts were greater than the monosalts, which is the same correspondence observed for the potassium salts. Cesium α -sulfostearic acid is another alkali metal salt that was studied.

An attempt was made to correlate the change in long spacing values of the acid salt of α -sulfostearic acid, $C_{16}H_{33}CH(SO_3M)CO_2H$, with the ionic radius of the alkali metal ion present. In general the long spacing value increases with increasing ionic radius of the alkali metal. Long spacing values increase in the order of lithium, potassium, cesium, and the corresponding ionic radii are .60, 1.33, 1.69 Å, respectively (2). However the sodium salt does not fit into this scheme. It gave the highest long spacing value even though its ionic radius, .95 Å, is smaller than that of potassium or cesium. This same pattern evolves if a comparison is made of the monosalts of α -sulfopalmitic acid. Without a detailed analysis of the crystal structure of these compounds it is impossible to explain the apparent abnormal behavior of the sodium salts.

Two divalent metals, magnesium and calcium, were studied. With these metals there was a greater tendency to form two phases than with the monovalent metals. An x-ray diffraction diagram from the mixed salt, sodium ammonium α -sulfostearate, showed this compound to have the shortest long spacing of any α -sulfostearate studied.

One salt with a large cation, the triethanolammonium ion, was investigated. The long spacing of triethanolammonium α -sulfostearic acid was less than that of the corresponding potassium salt, so the large group apparently affects the molecular packing.

An x-ray pattern of a detergent bar made by milling four parts of disodium α -sulfostearate with one part of triethanolammonium α -sulfostearic acid showed a super-position of the patterns of the two pure components. Investigation of a detergent bar made by neutralizing 20% of the acidity of sodium α -sulfostearic acid with triethanolamine in the milling process also showed the presence of two phases. However when sodium α -sulfostearic acid was 20% neutralized in the milling process the pattern for sodium ammonium α -sulfostearate was completely lacking and only that for the monosodium salt was observed. A more thorough investigation with particular attention to a wider range of compositions will be required before conclusions may be drawn concerning the structure of such detergent bars.

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